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Synthesis and X-Ray Structure of a Borohydrido Metallocene of Neodymium and its Use as Pre-catalyst in Nd/Mg Dual-Component Ethylene and Isoprene Polymerisations.

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Abstract

$\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$ (**1**) ($\text{Cp}^* = \text{C}_5\text{Me}_5$) has been readily obtained in one step from $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ and fully characterized by ^1H NMR, IR spectroscopy, and elemental analysis. Its X-Ray structure displays a neutral monomeric complex, bearing one slightly distorted terminal BH_4 group. Associated to $n\text{BuEtMg}$, **1** affords a highly active catalyst for ethylene polymerisation, the first one prepared from a borohydrido organolanthanide pre-catalyst. In the same experimental conditions, the catalytic behaviour of **1** is similar to that of previously described $\text{Cp}^*_2\text{NdCl}_2\text{Li}(\text{Et}_2\text{O})_2$ (**2**). The **1**/ $n\text{BuEtMg}$ system is not deactivated even in the presence of large excesses of THF. In contrast to its chloro homologue **2**, the addition of 1 equivalent of $n\text{BuEtMg}$ to **1** affords a catalyst for a *trans*-selective polymerisation of isoprene.

1. Introduction

The potential of lanthanide derivatives for polymerisation catalysis is nowadays well established. They have been successfully used towards ethylene and α -olefins, dienes, polar monomers, also enabling statistic or block co-polymerisation [1-4].

After the pioneer work of Ballard [5] and Watson [6], Marks reported in 1985 that lanthanide hydrides $(\text{Cp}^*_2\text{LnH})_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$), and particularly those of early lanthanides (La, Nd, Sm) display a tremendous activity towards ethylene polymerisation [7]. This activity, extremely high according to Gibson's scale [8], could be compared to that of homogeneous Ziegler Natta group 4 catalysts. Such results prompted, until now, a great number of research groups to explore the field of ethylene polymerisation with lanthanide-based catalysts. As reviewed recently [9], almost all of them display at least one Ln-hydride or Ln-alkyl bond, and divalent derivatives can be used alternatively for the same purpose. Among these complexes, lanthanidocenes remain by far the most active. Because of the presence of this reactive bond, lanthanide complexes can proceed as single-component catalysts, which is still reported as an advantage in comparison with group 4 catalysts which require an aluminium-based activator in general in large excess.

However, such compounds display several drawbacks: first, they are not only extremely sensitive to oxygen and moisture, and therefore difficult to handle, but they are also thermally unstable and sometimes reactive with solvents or even silicon grease [10, 11]. Second, the polymerisation experiments carried out with these complexes do not generally proceed in a living manner. For example the "historical" $(\text{Cp}^*_2\text{NdH})_2$ gives rise to a polymerisation process that deactivates very fast, and finally a low productivity is obtained [1, 7].

Another strategy, the one developed in our group, consists of the *in situ* generation of the highly reactive alkyl species, by direct addition of an alkylating reagent to a pre-catalyst [12]. Several years ago, we [13-15] and another group [16], succeeded in polymerising ethylene by using chlorolanthanidocenes in combination with dialkylmagnesiums. More recently, we showed that lanthanide alkoxides could also advantageously be activated in the same fashion [17]. Moreover, it was observed that in the presence of an excess of dialkylmagnesium, a real catalysis takes place, in a controlled-living manner, *via* reversible transfer reactions between lanthanide and magnesium. Boisson *et al.* extended this concept to several chlorometallocenes of neodymium, activated with Mg or Al/Li co-reagents [18]. Apart from these examples of dual-component catalysts, very few other lanthanide-based pre-catalysts were reported as efficient, though poorly, for ethylene polymerisation, namely: $[\text{NON}]\text{YCl}(\text{THF})_2$ ($\text{NON} = \text{bis}(\text{syilamido})\text{biphenyl}$) [19], $(\text{C}_5\text{H}_4)\text{Nd}(\text{MS})_2(\text{PzA})_2$ ($\text{MS} = \text{CH}_3\text{SO}_3$; $\text{PzA} = \text{pyrazinamide}$) [20], and adducts $(\text{C}_5\text{H}_4)\text{TbBr}_2(\text{L})$ ($\text{L} = \text{pyrazole}$ or PPh_3) [21], all in the presence of MAO. A series of calixarene lanthanide complexes

were also reported as moderately efficient in the presence of $\text{Al}(i\text{Bu})_3$ [22]. In summary and as far as we know, five kinds of lanthanide-X groups can be, to date, activated successfully by an alkylating agent towards ethylene polymerisation: $[\text{Ln}]\text{-Cl}$, $[\text{Ln}]\text{-Br}$, $[\text{Ln}]\text{-OR}$, $[\text{Ln}]\text{-OAr}$ and $[\text{Ln}]\text{-OSO}_2\text{CH}_3$. The efficiency of this *in situ* approach led us to expand it to other pre-catalysts, which would just need to be activated directly in the reaction mixture, in order to generate a Ln-R bond and provide an active catalyst.

Our purpose was therefore to examine the ability of a borohydrido lanthanide complex as pre-catalyst for ethylene polymerisation, and the role of the BH_4 group in such catalysis. Considering that best performances are obtained with bis-pentamethylcyclopentadienyl derivatives, we thus synthesized the borohydridometallocene $\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$ (**1**), which was found monomeric according to X-Ray studies. We then studied the behaviour of this complex towards ethylene polymerisation, in the presence of an alkylating agent as co-catalyst. The results are compared to those obtained with the chloro complex $\text{Cp}^*_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2$ (**2**). With the aim to get a full evaluation of performance between the Ln-Cl and the $\text{Ln}(\text{BH}_4)$ moiety *vs.* polymerisation, we also investigated and compared both complexes towards isoprene polymerisation, which will show that surprisingly, the BH_4 moiety behaves differently from the chloride ligand.

2. Results and Discussion

2.1. Synthesis and characterization of $\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$ (**1**).

Toluene soluble $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ are useful precursors for organolanthanides syntheses, alternatively to the traditional trichlorides [23-25]. Moreover, $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ allowed the formation and isolation of very scarce examples of early half-lanthanidocenes, which are generally not isolable in the case of chloro homologues, the latter easily undergoing comproportionation reactions [26].

Starting from the soluble precursor $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$, $\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$ (**1**) is readily obtained in high yield in one step (Eq. 1).

((Equation 1))

We had already used this strategy to prepare the complexes $(\text{Cp}^{4i})_2\text{Ln}(\text{BH}_4)$ and $(\text{Cp}^{4i})\text{Ln}(\text{BH}_4)_2(\text{THF})$ ($\text{Ln} = \text{Sm}, \text{Nd}$; $\text{Cp}^{4i} = \text{C}_5\text{H}_i\text{-Pr}_4$) [23]. Usually, the synthesis of borohydrido

complexes of early lanthanides proceeds in two steps, via salt metathesis starting from LnCl_3 or its THF adduct, followed by the subsequent substitution of the last chloride by a borohydride (Eq. 2) [27, 28]. One drawback of this synthetic pathway is the presence of chloride anions in the reaction medium, which may lead to the isolation of less soluble chloride-contaminated derivatives [29].

((Equation 2))

Despite the paramagnetism of neodymium, the ^1H NMR spectrum of **1** can be easily interpreted (Figure 1). The BH_4 signal is a typical broad one (due to simultaneous H-B coupling and intrinsic paramagnetism) and it can be integrated as expected (4H/30H) with respect to the Cp^* signal. The borohydride resonance appears at 35.1 ppm; this value is far from the one found for other borohydrido-neodymocene compounds: $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3)_2\text{Nd}(\text{BH}_4)$ ($\delta = 74$ ppm) [28] and $(\text{Cp}^{4i})_2\text{Nd}(\text{BH}_4)$ ($\delta = 74.4$ ppm) [23]. However, it is well-known that ^1H NMR data of paramagnetic lanthanide complexes dramatically depend on their molecular structure [30]. Actually, the metal bears two additional ether ligands in $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3)_2\text{Nd}(\text{BH}_4)$ and none in $(\text{Cp}^{4i})_2\text{Nd}(\text{BH}_4)$. It is worth noting that for the tetra-coordinated complexes $(\text{cot})\text{Nd}(\text{BH}_4)(\text{THF})_2$ ($\text{cot} = \text{C}_8\text{H}_8$) and $(\text{C}_4\text{Me}_4\text{P})_2\text{Nd}(\text{BH}_4)_2^-$, the BH_4 signal is found at $\delta = 44$ ppm [31] and $\delta = 49$ ppm (solvent TDF) [24], respectively. The signals of THF in **1** are depicted at -11.7 and -34.9 ppm, a quite usual range for a molecule of THF that is coordinated to the neodymium atom [32].

((Figure 1))

1 was found to be a neutral monoborohydride complex, as generally observed for borohydrido organolanthanides, even in the case of the larger early ones [23, 27, 33]. This has been attributed to the more electron donating ability of the BH_4 than that of the chloride [10]. In contrast, halide analogues often display an anionic, “ate” molecular structure [34], as exemplified by the well-known $\text{Cp}^*_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2$ [35]. A few examples of anionic bisborohydride metallocene-like complexes were described for the early series but they bear poor electron donating ligands [24, 25]. IR analysis of complex **1** shows two major absorbances (2430 and 2111 cm^{-1}), typical of the terminal $\text{Nd}(\mu_3\text{-H})\text{B-H}$ borohydride moiety found in monomeric complexes [36]. Minor absorbances were also observed (2282 , 2216 , 2186 , 2160 cm^{-1}); they could be ascribed to a distorted tridentate BH_4 mode as already discussed [37].

2.2. X-Ray structure of **1**:

The X-Ray crystallographic study of **1** revealed, as expected from ^1H NMR data, a tetrahedral monomeric structure (Fig. 2) [38]. The asymmetric unit contains two molecules. The samarium analogue of **1**, $\text{Cp}^*_2\text{Sm}(\text{BH}_4)(\text{THF})$, synthesized in two steps (see above), displays a very similar structure [27] but in that latter case, the hydrogen atoms of the tetrahydroborate ligand could not be located, thus preventing an exact description of the inner coordination sphere of the central samarium atom. In addition, no polymerisation data were reported with this samarium complex (see further). With respect to samarium, all distances are slightly longer, as expected in the case of larger neodymium [39]. All bond lengths and angles associated with the cyclopentadienyl ligand and the metal ion are unexceptional.

((Figure 2))

The Nd-O distance is typical of a mono THF neodymium solvate [23]. The Nd-B distance (2.63(5) and 2.66(4) Å for each molecule) is in accordance with a terminal tridentate BH_4 [40], whereas the hexameric $[\text{Cp}^{*'}\text{Nd}(\text{BH}_4)_2]_6$ ($\text{Cp}^{*'} = \text{C}_5\text{Me}_4n\text{Pr}$) displays 2.7-2.9 Å BH_4 bridges [29]. In one of the two molecules of the asymmetric unit, the three hydrogen atom bridges are quite identical, Nd1-H: 2.50(6), 2.52(3), 2.54(1). In the second one, significant differences are observed, Nd2-H: 2.21(3), 2.30(9), 2.57(0), 3.79(2). Also, whereas the bond angles are equivalent in Nd1-H-B (72.2(9), 72.4(2), 71.0(7), those found in Nd2-B-H (54.9(7), 59.5(5), 72.2(4) °) are significantly different. These geometric features are consistent with one regular tridentate BH_4 (first molecule in the asymmetric unit) and one distorted mode of BH_4 group (second molecule), and they agree well with the observations made by infra-red spectroscopy.

2.3. Ethylene polymerisation:

Ethylene polymerisation catalysts made of Ln/Mg combinations have been extensively studied with chlorolanthanidocenes [14, 15] and lanthanide alkoxides [17] in our laboratory. We report in the present paper that **1**, the first time for a borohydrido complex of lanthanide, affords a very powerful ethylene polymerisation catalyst when combined with BEM ($n\text{BuEtMg}$, heptane solution). Selected experiments are gathered in Table 1.

((Table 1))

In all experiments, the same profile of monomer consumption is observed (see the curves in the supplementary material section): first a steady stage, followed by a rapid increase of activity (A_{\max}) which then progressively falls down. Such a decrease of activity was already noticed with single component initiators [7], and also in the case of dual component systems [15, 18]. The extent of the first stage depends on the Mg/Nd ratio and the corresponding activity, though much lower than during the second stage, remains “high” according to Gibson’s scale [8]. In the presence of 10 equivalents of BEM, A_{\max} reaches 4100 kg PE/mol Nd/h (run 1), but this maximum is observed at $t = 1$ min. With 50 equivalents of BEM, the first stage lasts ca. 10 minutes (run 2). Considering the time of ethylene consumption, the productivity is 50 kg PE/mol Nd for run 1, whereas it reaches 500 kg PE/mol Nd in the presence of 50 equivalents of BEM (run 2). The maximum of activity is 4700 kg/mol Nd/ h ($t = 12$ min) in that latter case.

Such a behaviour compares well with that of chlorometallocenes of lanthanides in the presence of Mg co-catalyst, already described and elucidated in our group [14]: 1) propagation of the polymerisation by means of the neodymium active species with fast reversible transfer between Nd and Mg (first stage); 2) increase of activity after a given time, corresponding to a lack of bimetallic interactions (second stage). In order to compare the influence of Cl^- vs BH_4^- as leaving group in the pre-catalyst, we carried out, in our conditions, a polymerisation experiment with $\text{Cp}^*_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2$, **2**, the chloro homologue of **1** (run 3). As shown in table 1 and activity vs time curve (see supplementary material section), both A_{\max} and productivity reach approximately the same values. One can conclude that, in the presence of an excess of Mg co-catalyst, both systems are roughly equivalent, involving probably the same trivalent $\text{Cp}^*_2\text{Nd-CH}_2\text{CH}_2\text{R}$ active species. Thus, a BH_4 group compares well with a Cl one in such catalytic systems. A proposed mechanism involving the different steps of the process is depicted in scheme 1.

((Scheme 1))

When a very large excess of BEM is added to neodymium pre-catalyst **1**, the time for maximum activity is shifted to ca. 150 min (2400 kg/mol Nd/ h). During this extended steady stage, a noticeable activity [8] is still observed (100 kg PE/mol Nd /h) and the overall productivity is 800 kg PE/mol Nd (run 4). In all cases, molecular weights and polydispersity indexes are in accordance with theoretical values taking into account the reversible chain transfer (Scheme 1, c) from Nd to Mg. These data are also typical of a single site type catalysis.

While it was reported that the presence of two THF per Sm sensibly lowers the activity of Cp^*_2Sm vs. ethylene [41] no great difference of activity and productivity is observed with 50 equivalent of THF in our case (run 5). One can only notice the shift of A_{\max} to earlier times, corresponding to the

shortening of the steady ethylene consumption period. MgR_2 is then acting as a scavenger for THF with respect to the Nd active species. Under such conditions, reversible interactions between Nd and Mg centers might be hindered, due to the coordination of THF to Mg. Actually, addition of 1000 equivalent of THF are necessary to observe a significant decrease of both activity and productivity (run 8). Finally, the system is completely deactivated in the presence of 5000 THF per Nd.

2.4. Isoprene polymerisation:

In a previous study, we found that the borohydrido $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ and the mono pentamethylcyclopentadienyl $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_2$ complexes were very efficient for isoprene polymerisation when combined to MgR_2 reagents [42, 43]. Both catalysts afford highly *trans*-stereoregular polyisoprene; this was correlated to the probable formation of bridged bimetallic $[\text{Nd}](\mu\text{-BH}_4)(\mu\text{-R})[\text{Mg}]$ active species. On the other hand, Cp^*_2LnX metallocenes are known to be quite inactive towards conjugated dienes polymerisation, due to the formation of a quasi-inert $\text{Cp}^*_2\text{Ln}(\text{allyl})$ compound [41]. Surprisingly, preliminary isoprene polymerisation studies show that the **1**/BEM combination displays some activity, giving 56 % conversion in 90 h at 50 °C, and a polymer that is 87 % *trans*-regular. Using **2** in place of **1**, no polymer was isolated.

^1H NMR monitoring shows that precatalyst **2** is totally alkylated by the reaction with 1 equivalent of BEM, as shown by the disappearance of the initial Cp^* signal ($\delta = 9.25$ ppm) to give two new resonances at 8.8 and 9.9 ppm. On the other hand, addition of the same quantity of BEM to **1** affords 50 % of alkylation with a broad Cp^* signal in the range $\delta = 8.7 - 8.9$ ppm and 50 % unreacted **1**. In the presence of 2 equivalents of BEM, 75 % of **1** is consumed. This points out the difficulty to displace a BH_4 group in a borohydrido neodymium compound **with respect to Cl in the chloro homologues**.

A tentative of rationalisation is presented in Scheme 2: after reaction with BEM, the resulting alkylated compound and unreacted **1** may be in equilibrium with a $[\text{Nd}](\mu\text{-BH}_4)[\text{Mg}]$ bimetallic species which would be the real active one. After isoprene insertion, the presence of the borohydride group in the coordination sphere of the neodymium atom, would promote $\eta^3\text{-}\eta^1$ allylic rearrangement of the ending unit of the growing polymer, hence leading to active catalytic species. Moreover, such a reaction scheme also argues for a *trans*-selective process, as previously reported with $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_2/\text{BEM}$ and $\text{Nd}(\text{BH}_4)_3(\text{THF})_3/\text{BEM}$ (see above).

((Scheme 2))

3. Conclusion

We report therein the first example of ethylene polymerisation catalysis from a borohydrido organolanthanide. The monomeric $\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$, simply available in one step from $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$, provides a highly active catalyst when combined with butylethylmagnesium (BEM), even in the presence of large excesses of THF. In the presence of a stoichiometric amount of BEM, $\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$ also allows *trans*-selective polymerisation of isoprene, in sharp contrast with its chloro homologue.

The approach which consists of an *in situ* alkylation of a pre-catalyst is an alternative method for the synthesis of catalytic species for polymerization, that is particularly well suited to borohydrido lanthanide complexes.

Finally, $\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$ represents a very rare example of compound that can be involved in catalytic systems for both ethylene or isoprene polymerisations. Ethylene-isoprene copolymerisations with the same pre-catalyst, and using the strategy described in this paper, are in progress.

4. Experimental

All operations were performed under argon using standard vacuum line techniques or in an argon-filled glove box ($\text{O}_2 < 2$ ppm). Solvents were stored over sodium/benzophenone ketyl and transferred by distillation to reaction vessels. BEM (butylethylmagnesium, 20 % solution in heptane) was purchased from Texas Alkyl. Cp^*H ($\text{Cp}^* = \text{C}_5\text{Me}_5$) was purchased from Aldrich. $\text{NdCl}_3(\text{THF})_2$ was a gift of Rhodia Electronics and Catalysis. $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ [44] and $\text{Cp}^*_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2$ (**2**) [35] were prepared as previously described.

NMR spectra were recorded on Bruker AC200 or Avance 300 spectrometers at 300 K (^1H , 200 and 300 MHz referenced to external TMS; ^{11}B , 96 MHz and referenced to external $\text{BF}_3\cdot\text{OEt}_2$). IR spectrum was recorded by diffuse reflectance mode on a Nicolet 460 FTIR device equipped with a MCT detector. Elemental analyses were obtained with a Fisons EA 1108 CHON apparatus at the Service d'Analyses de l'Université de Dijon.

4.1. Synthesis of $\text{Cp}^*_2\text{Nd}(\text{BH}_4)(\text{THF})$ (**1**).

In the glovebox, a flame dried vessel was charged with 360 mg (0.89 mmol) of $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ and a slight excess (330 mg; 1.90 mmol) of Cp^*K . The vessel was then connected to a vacuum line and THF (30 mL) condensed at $-78\text{ }^\circ\text{C}$. The mixture was allowed to warm up to room temperature and stirred for 16 h. The solvents were removed in vacuum, leaving a pale blue solid. This crude material was extracted three times with pentane (3 x 25 mL), and the blue solution was filtered. The filtrate was concentrated to ca 1 mL, affording a blue microcrystalline powder. The solid was isolated by decantation, washed with cold pentane, and dried 4 h at room temperature (yield 350 mg, 78.5 %). ^1H NMR (C_6D_6): δ 35.1 (br, $\Delta\nu = 400\text{ Hz}$, 4H, BH_4), 9.77 (s, 10H, C_5Me_5), -11.7 (br, $\Delta\nu = 250\text{ Hz}$, 4H, THF) and -34.9 (br, $\Delta\nu = 300\text{ Hz}$, 4H, THF). ^{11}B NMR (C_6D_6): δ 100.4. IR (nujol): ν (cm^{-1}) = 2430 (vs), 2282 (w), 2216 (w), 2186 (m), 2160 (w), 2111 (s). Anal. Calc. for $\text{C}_{24}\text{H}_{42}\text{BONd}$: C, 57.48; H, 8.38. Found: C, 57.26; H, 8.65.

^1H NMR experiments: in the glove box, 7 mg of **1** (14 μmol) were weighed in a NMR tube equipped with a teflon stop-cock. C_6D_6 (0.4 mL), then 1 equivalent of BEM (9 μL), were added. The ^1H NMR spectrum, recorded immediately, showed the presence of a broad new Cp^* resonance ($\delta = 8.7\text{--}8.9\text{ ppm}$) besides the one of complex **1**, still present. The two signals were in a 1:1 ratio. After addition of one additional equivalent of BEM (9 μL), both signals were still present but in a *ca.* 3:1 ratio in favour of the new one. The same experiment, conducted with **2** (9 mg, 14 μmol) and one equivalent of BEM, showed the complete disappearance of the Cp^* resonance of **2** ($\delta = 9.25\text{ ppm}$) and the presence of two new signals (8.8 and 9.9 ppm in a 1:2 ratio).

4.2. X-ray data collection and processing

Crystals of **1** were grown in pentane. Data were collected on a Bruker SMART 1K CCD diffractometer using Mo- $\text{K}\alpha$ graphite-monochromated radiation ($\lambda = 0.71073\text{ \AA}$). Temperature was held constant at 100 K with an Oxford Cryostream 700 low temperature device. The structure was solved by direct methods using SIR97 [45] and refined by full matrix least-square techniques using the JANA2000 program [46]. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 270348 for compound **1**.

4.3. Ethylene polymerisation

In a typical experiment (run 1), the anhydrous and degassed solvent (toluene, 18 mL) was placed in a thermostatic ($90\text{ }^\circ\text{C}$) glass vessel equipped with a stainless steel blade. Ethylene inlet

allowed to saturate continuously the inner medium at 1.1 bar. A solution of precatalyst **1** (2 mg, 4 μmol) and BEM, diluted in 2 ml toluene, was prepared in the glove box, and injected into the polymerisation reactor. The ethylene consumption was then monitored with a flowmeter. The polymerisation medium was always homogeneous. At the end of the run (10 min after the catalytic mixture injection), the polymer was recovered by precipitation in a large excess of acidified methanol (100 mL). The polymer was then filtered, washed with pure methanol, dried, and weighed (0.18 g). The same procedure was carried out for runs **2 to 6** using conditions given in table 1.

4.4. Isoprene polymerisation

10 mg (0.02 mmol) of catalyst precursor **1** were weighed in a glovebox, in a 20 mL flask. Dry toluene (0.5 mL), BEM (0.014 mL, as a 20 % solution in heptane), and freshly distilled isoprene (0.5 mL, 5 mmol), were added in this order via syringes into the flask. The reaction mixture was magnetically stirred at 50 °C for a given time. The polymerisation reaction was terminated as follows: the viscous mixture was diluted in standard toluene (1 mL) and the resulting solution was poured into ethanol. The white polymer was filtered out, and dried under vacuum for 24 h. Yield: 190 mg (56 %); ^1H NMR: 87.3 % *trans*-1,4, 10.7 % 3,4, 2 % *cis*-1,4.

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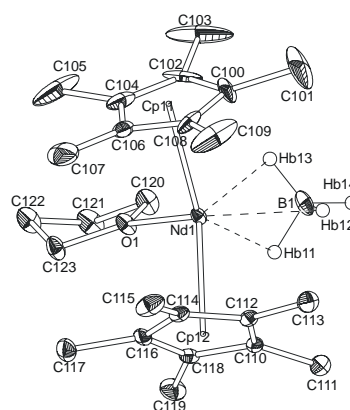
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- [38] *Crystal Data*: C₂₄H₄₂BNdO, *M* = 501.63, triclinic, space group *P*-1(*N*^o. 2), *a* = 8.524(2), *b* = 17.221(4), *c* = 18.399(4) Å, α = 62.956(3), β = 88.749(3), γ = 86.141(3) °, *V* = 2400(2) Å³, *Z* = 4, *D*_{calc} = 1.388 gcm⁻³, μ (Mo-K α) = 2.174 mm⁻¹, *F*(000) = 1036, crystal size 0.10 x 0.12 x 0.15 mm. *T* = 100 K, 17501 reflections collected, 9725 unique, 487 parameters. Final *R* values (*I* > 3 σ (*I*)) : *R* = 0.0393, *wR* = 0.0391. The hydrogen atoms bound to carbon were placed in idealized positions [C–H = 1.00 Å, *U*_{iso}(H) = 1.2 x *U*_{iso}(C)], while hydrogen bound to boron were located in a difference Fourier map and included (with isotropic thermal parameter) in the refinement. The structure was refined (weighted least squares refinement on *F*) to convergence.
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Graphical abstract

Monomeric $\text{Cp}^*_2\text{NdBH}_4(\text{THF})$ has been synthesized and fully characterised.

Combined with butylethylmagnesium (BEM), it gives rise to a powerful ethylene polymerisation catalyst, the first one made of a borohydrido organolanthanide. $\text{Cp}^*_2\text{NdBH}_4(\text{THF})/\text{BEM}$ also allows isoprene polymerisation, in contrast with the corresponding chloro neodymocene.



Captions.

Figure 1. ^1H NMR spectrum of **1** (C_6D_6 , 300 K)

Figure 2. Molecular structure of **1** in the crystal (one of the two molecules of the asymmetric unit). Selected bond lengths (\AA) and angles ($^\circ$): Nd-O 2.48(9) , Nd-B 2.63(5), Nd-CP (CP is the centroid of Cp^*) 2.48(1) and 2.48(2), CP-Nd-CP 133.18.

Scheme 1. Ethylene polymerisation mechanism with **1**/excess MgR_2 catalytic system: (a) catalyst generation; (b) propagation; (c) reversible transfer.

Scheme 2. Possible isoprene polymerisation mechanism with **1**/1 MgR_2 showing σ - π allyl rearrangement promoted by $\text{RMg}(\text{BH}_4)$ (PI = polyisoprene chain, THF omitted for clarity)

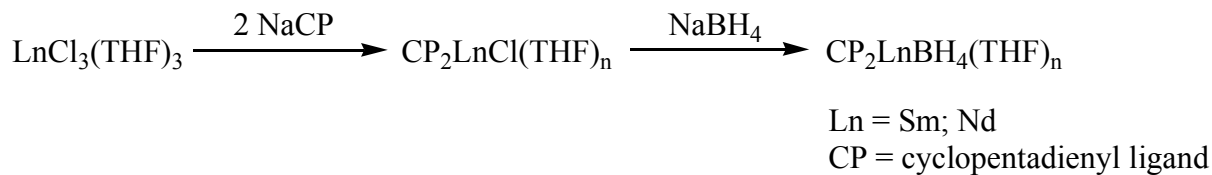
Table 1. Ethylene polymerisation with borohydrido complexes of neodymium/ BEM.^a

Supplementary material.

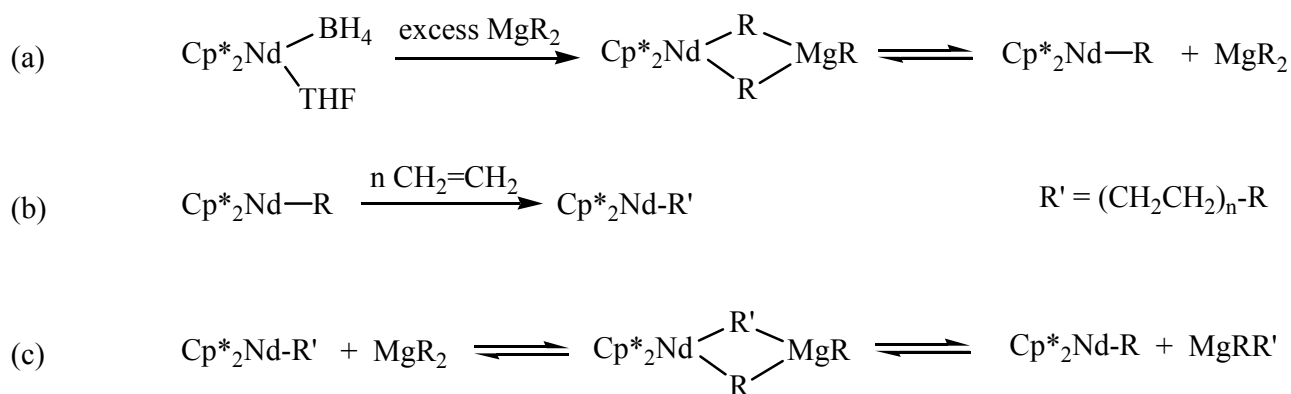
Figure 3. Activity vs. time plot observed with the **1**/50 BEM (run 2) and **2**/50 BEM systems (run 3) (4 μmol pre-catalyst, 90 $^\circ\text{C}$, 20 mL toluene, 1.1 atm ethylene kept constant).



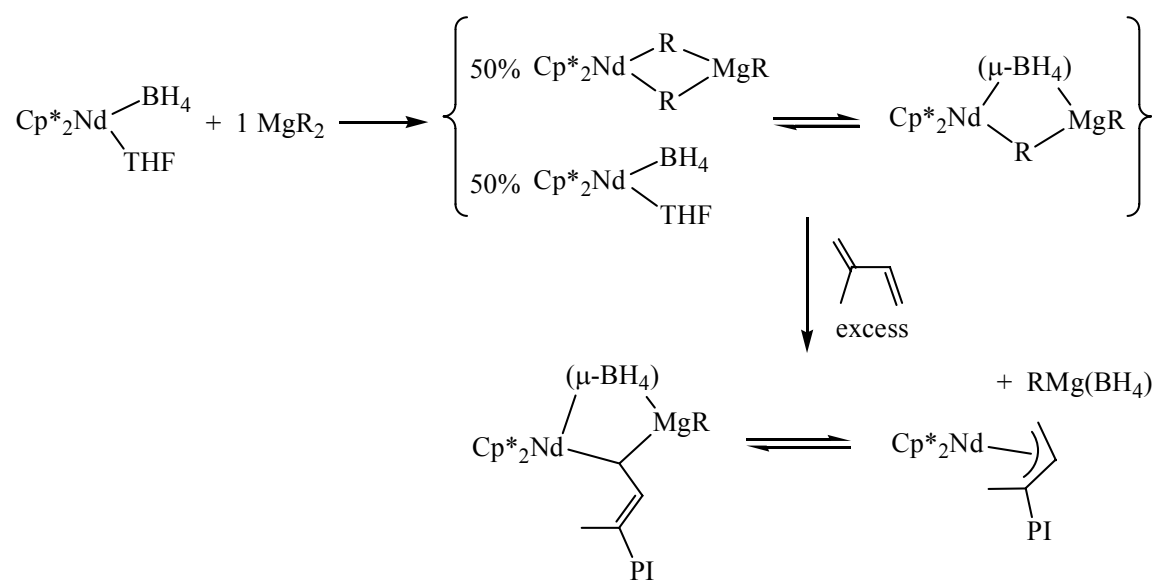
Equation 1



Equation 2



Scheme 1



Scheme 2

Table 1: ethylene polymerisation with borohydrido complexes of neodymium/ BEM.^a

run	catalyst	time (min)	yield (g PE)	A_{\max} (kg PE/mol Nd/h)	\overline{M}_n	(<i>PDI</i>)
1	1 /10BEM	2	0.18	4000	2900	1.76
2	1 /50BEM	28	2.39	4860	5000	1.46
3	2 /50BEM	20	1.30	4300	3600	1.46
4	1 /250BEM	185	3.15	2400	2500	1.35
5 ^b	1 /50BEM	17	2.2	4000	5100	1.57
6 ^c	1 /50BEM	>30	0.8	800	2200	2.0

^aP_{ethylene} = 1.1 atm, T = 90 °C, V(toluene) = 20 mL, [Nd] = 2 · 10⁻⁴ molL⁻¹. ^b In the presence of 50 equiv. of THF. ^c In the presence of 1000 equiv. of THF.